

Magnetism chills out

Materials that behave as magnetic refrigerants have surprisingly complex structures

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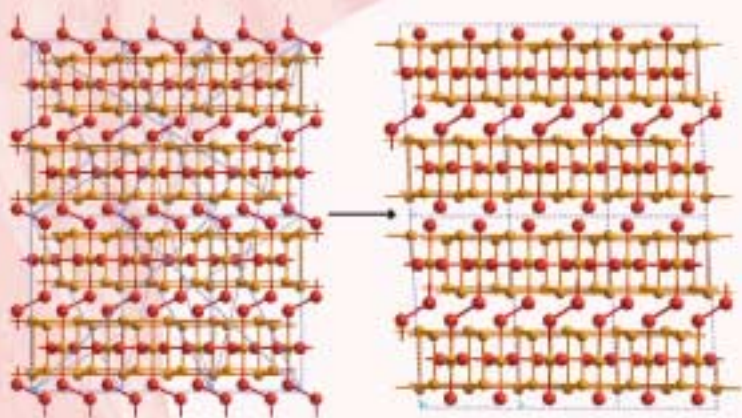


Figure 1
The transition from monoclinic to orthorhombic structure in the alloy, $Tb_3Si_2Ge_2$. The red balls are silicon or germanium atoms, yellow balls represent terbium atoms. The arrow marks where a strong shear movement leads to breaking of the silicon or germanium bonds

When a magnetic field is applied to a magnetic material, the constituent magnetic moments align, and the material warms up. When the field is switched off, the moments become disorderly again and the material cools. In certain alloys, this magnetocaloric effect is substantial – large enough to suggest a novel type of refrigeration based on cycling the magnetic field-switching and allowing the heat given off to escape. Companies are already interested in applying this environmentally-friendly technology to air-conditioning and supermarket chillers.

The giant magnetocaloric effect was first discovered in 1997 in the gadolinium silicon germanium alloy, $Gd_5(Si_{1-x}Ge_x)_4$, and has since been found in similar metal compounds. A field of 1 tesla (20,000 times the Earth's field) can produce a change of 3 to 4 degrees in these materials, and depending on the proportion of germanium contained, the effect can be tuned to appear across a range of temperatures between 20 and 295K.

The extent of the magnetocaloric effect is believed to depend on an intimate coupling between the material's crystal structure and its magnetism. X-ray and magnetisation measurements indicate that as the temperature drops, a strong magnetic moment

appears alongside a change in crystal structure from monoclinic to orthorhombic. Figure 1 shows how bonds between silicon or germanium atoms of every second layer break, allowing the layers to shift sideways to a new structure.

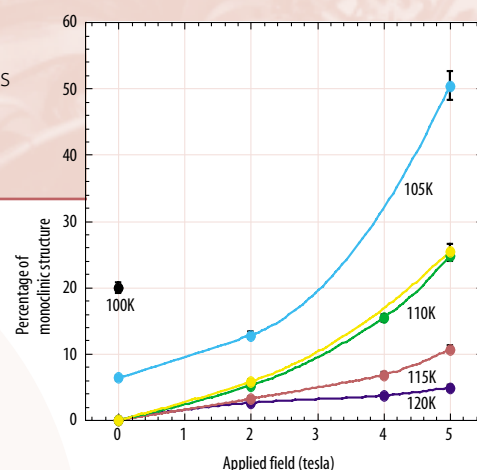


Figure 2
The percentage of monoclinic phase induced by increasing the magnetic field at selected temperatures as determined from high-resolution D2B data

Changing phases

The obvious question is whether the structural transition strictly coincides with the onset of magnetism, and if so which triggers which. We set about finding out using neutron diffraction. We chose a variant of the alloy containing terbium rather than gadolinium because the latter strongly absorbs neutron energy; the terbium compound still shows the magnetocaloric effect.

Starting at a temperature of 110K, well above the magnetic transition temperature, we found that applying a field as high as 5 tesla induced little change from the monoclinic to the orthorhombic structure (figure 2). Even when lowering the temperature to 105K, only half the sample changed. But what was surprising was that the magnetic scattering pattern obtained indicated that the remaining monoclinic phase had become magnetic as well.

To explore this unexpected magnetic phase, we decided to do a slow and detailed scan with an intense neutron beam, in a zero field, lowering the temperature at a rate of about 2 degrees an hour. The resulting diffraction pattern in figure 3 shows the magnetic peaks for the monoclinic (M) and orthorhombic (O1) structures, revealing that magnetism first emerges in the former and only at about 104K does the latter appear. The monoclinic peaks disappear at about 92K, marking completion of the structural transition. We also found that the monoclinic phase was largely ferromagnetic, similar in nature to the magnetic structure of the orthorhombic phase. Neutron studies are the only way that could distinguish between the two magnetic phases.

Clearly, these results are significant in understanding the magnetocaloric effect. The magnetic phase transition happens at a higher temperature (about 112K) than the structural phase transition (about 105K). Even an applied field of 5 tesla could not induce the change of more than 50 per cent in the crystal structure, showing that the interplay between crystal structure and magnetic properties is more complex than previously thought. ■

Figure 3
Neutron diffraction contour plot of $Tb_3Si_2Ge_2$ in a selected angular and temperature range as recorded on the high-intensity D1B diffractometer. The diffraction peaks marked are of purely magnetic origin coming from the monoclinic (M), the orthorhombic (O1), or both crystallographic structures

